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**(54) AGENT DE RECOUVREMENT COMPOSE D'AU MOINS 3
CONSTITUANTS, PROCEDE PERMETTANT DE LE
PREPARER ET UTILISATION**

**(54) COATING COMPOSITION COMPRISING AT LEAST 3
COMPONENTS, PROCESS FOR ITS PREPARATION, AND ITS
USE**

(57) L'invention concerne un agent de recouvrement composé d'au moins trois constituants (I), (II) et (III), qui se caractérise en ce que le constituant (I) contient comme liant (A), au moins un copolymérisat acrylate (A1) dispersé ou dissous dans un solvant organique, éventuellement diluable dans l'eau, et dont le poids moléculaire moyen en nombre Mn se situe entre 1000 et 30000 Dalton, son indice d'hydroxyle étant compris entre 40 et 200 et son indice d'acide, entre 5 et 150, et/ou une résine polyester (A2) dispersée ou dissoute dans un solvant organique, éventuellement diluable dans l'eau, dont le poids moléculaire moyen en nombre Mn se situe entre 1000 et 30000 Dalton, son indice d'hydroxyle étant compris entre 30 et 250 et son indice d'acide, entre 5 et 150, et/ou une résine polyuréthane (A3) dispersée ou dissoute dans un solvant organique, éventuellement diluable dans l'eau, dont le poids moléculaire moyen en nombre Mn se situe entre 1000 et 30000 Dalton, son indice d'hydroxyle étant compris entre 20 et 200 et son indice d'acide entre 5 et 150, et/ou éventuellement un autre liant (A4). Les constituants liants sont sélectionnés de manière qu'une solution à 50 % du liant (A) dans l'éthoxyéthylpropionate présente une viscosité de < = 6,0 dPa.s à 23°C. L'agent de recouvrement se caractérise également en ce que le constituant (II) contient comme réticulant au moins un polyisocyanate non bloqué, et que le constituant (III) contient les constituants (A1) et/ou (A2) et/ou (A3) et/ou (A4) en dispersion aqueuse.

(57) The invention concerns a coating agent which comprises at least three components (I), (II) and (III) and is characterized in that component (I), as binder (A), contains at least one acrylate copolymer (A1) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 40 and 200 and an acid number of between 5 and 150, and/or a polyester resin (A2) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 30 and 250 and an acid number of between 5 and 150, and/or a polyurethane resin (A3) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 20 and 200 and an acid number of between 5 and 150, and/or optionally a further binder (A4), the binder components being selected such that a 50 % solution of binder (A) in ethoxyethylpropionate has a viscosity of < = 6.0 dPa.s at 23°C. The coating agent according to the invention is further characterized in that component (II) contains at least one non-blocked polyisocyanate as crosslinking agent; and in that component (III) contains components (A1) and/or (A2) and/or (A3) and/or (A4) in an aqueous dispersion.



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**Coating composition comprising at least 3 components,
process for its preparation, and its use**

Field of the invention

5 The present invention relates to a coating composition comprising at least three components (I), (II) and (III) which is based on a hydroxyl-containing and acid-group-containing polymer which is dissolved or dispersed in one or more organic, optionally water-dilutable solvents, on one or more isocyanate group-containing crosslinking agents and on one or more dispersions of polymers containing hydroxyl and acid groups.

15 The present invention additionally relates to a process for the preparation of these coating compositions and to the use of the coating compositions in refinishing and for the coating of plastics and as topcoat or filler.

20 **Prior art**

Conventional, i.e. organically dissolved, coating compositions based on hydroxyl-containing binders and on isocyanate-group-containing crosslinking agents, which are employed in the area of automotive refinishing are usually multicomponent systems. One component contains the binder, optionally pigments and fillers, and customary auxiliaries and additives, while

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(54) Title: COATING AGENT COMPRISING AT LEAST THREE COMPONENTS, PROCESS FOR ITS PREPARATION AND ITS USE			
(54) Bezeichnung: AUS MINDESTENS 3 KOMPONENTEN BESTEHENDES BESCHICHTUNGSMITTEL, VERFAHREN ZU SEINER HERSTELLUNG SOWIE SEINE VERWENDUNG			
(57) Abstract			
<p>The invention concerns a coating agent which comprises at least three components (I), (II) and (III) and is characterized in that component (I), as binder (A), contains at least one acrylate copolymer (A1) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 40 and 200 and an acid number of between 5 and 150, and/or a polyester resin (A2) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 30 and 250 and an acid number of between 5 and 150, and/or a polyurethane resin (A3) which is dissolved or dispersed in an organic optionally water-dilutable solvent and has a number average molecular weight Mn of between 1000 and 30 000 Dalton, an OH number of between 20 and 200 and an acid number of between 5 and 150, and/or optionally a further binder (A4), the binder components being selected such that a 50 % solution of binder (A) in ethoxyethylpropionate has a viscosity of < - 6.0 dPa.s at 23 °C. The coating agent according to the invention is further characterized in that component (II) contains at least one non-blocked polyisocyanate as crosslinking agent; and in that component (III) contains components (A1) and/or (A2) and/or (A3) and/or (A4) in an aqueous dispersion.</p>			
(57) Zusammenfassung			
<p>Gegenstand der vorliegenden Erfindung ist ein aus mindestens drei Komponenten (I), (II) und (III) bestehendes Beschichtungsmittel, dadurch gekennzeichnet, daß die Komponente (I) als Bindemittel (A) mindestens ein in organischen, gegebenenfalls wasserlöslichem Lösungsmittel gelöstes oder dispergiertes Acrylatcopolymerat (A1) mit einem zahlenmittleren Molekulargewicht Mn zwischen 1.000 und 30.000 Dalton, einer OH-Zahl von 40 bis 200 und einer Säurezahl von 5 bis 150 und/oder ein in organischen, gegebenenfalls wasserlöslichem Lösungsmittel gelöstes oder dispergiertes Polyesterharz (A2) mit einem zahlenmittleren Molekulargewicht Mn zwischen 1.000 und 30.000 Dalton, einer OH-Zahl von 30 bis 250 und einer Säurezahl von 5 bis 150 und/oder ein in organischen, gegebenenfalls wasserlöslichem Lösungsmittel gelöstes oder dispergiertes Polyurethanharz (A3) mit einem zahlenmittleren Molekulargewicht Mn zwischen 1.000 und 30.000 Dalton, einer OH-Zahl von 20 bis 200 und einer Säurezahl von 5 bis 150 und/oder gegebenenfalls ein weiteres Bindemittel (A4) enthält, wobei die Bindemittelkomponenten so ausgewählt werden, daß eine 50-%ige Lösung des Bindemittels (A) in Ethoxyethylpropionat eine Viskosität von < - 6.0 dPa.s bei 23 Grad C aufweist, die Komponente (II) mindestens ein nichtblockiertes Polyisocyanat als Vernetzungsmittel enthält und die Komponente (III) die Komponenten (A1) und/oder (A2) und/oder (A3) und/oder (A4) in wässriger Dispersion enthält.</p>			



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the other component contains the crosslinking agent. In addition, an adjustment additive for adjusting the desired viscosity of the coating composition is also prepared, and consists essentially of a mixture of
5 various solvents.

However, for ecological and economic reasons the paint industry is attempting to replace as large as possible a proportion of the organic solvents employed in coating materials by water. In the finishing of
10 automobiles in particular there is a great requirement for aqueous coating materials. This applies both to the area of production-line autofinishing and to the area of automotive refinishing.

In these areas, aqueous coating compositions
15 are employed in particular in the topcoats sector. Topcoats in this context are understood as being coating materials which are used to produce the topmost coat of paint. This topmost coat of paint may consist of one or more layers, and may in particular be two-
20 layer. For single-layer topcoats, especially for solid-color finishes, use is nowadays made predominantly of binders based on hydroxyl-containing polyacrylates in conjunction with pigments, which are crosslinked with di- and/or polyisocyanates. Two-layer topcoat systems
25 consist of a pigmented basecoat and of a clearcoat which is unpigmented, or pigmented only with transparent pigments, which is applied over the basecoat, and which again predominantly contains binders based on hydroxyl-containing polyacrylates and

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is crosslinked with di- and/or polyisocyanates.

Two-coat finishes are nowadays produced by the wet-on-wet technique, in which a pigmented basecoat is first applied and the resulting basecoat is coated over, without a baking step but with pre-drying, with a clearcoat, basecoat and clearcoat subsequently being cured together. This technique places high requirements on the basecoat and the clearcoat. The clearcoat applied over the basecoat must not start to dissolve the basecoat, since otherwise finishes of poor appearance are obtained. This technique is employed in particular for finishes where basecoats containing special-effect pigments (e.g. metal pigments, especially aluminum flakes or pearlescent pigments), are employed. The clearcoat brings about a good appearance (good evenness, high gloss, low boil-mark tendency, good topcoat holdout and high hardness) and also good weathering resistance.

In the area of automotive refinishing, moreover, there is the additional requirement that the coating compositions employed are fully curable at low temperatures (in general < 80 degrees C) and, even when cured at these low temperatures, lead to films having the good mechanical properties required.

EP-B-358 979 discloses aqueous two-component polyurethane coating compositions comprising a hydroxyl-containing polyacrylate resin, which is dispersed in water, and a polyisocyanate component. These coating materials described in EP-B-358 979,

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however, exhibit great disadvantages in respect of gloss, relaxation (low graininess of the coating), boil-mark tendency and, as a result of this, spray safety, and in respect of weathering resistance,
5 especially in respect of resistance to long-term condensation conditions (40 degrees C, 240 hours), processability (drop in viscosity and inadequate pot life) and hardness.

Moreover, DE-B 25 07 884 discloses a process
10 for the preparation of aqueous coating compositions, in which first of all a solution of a carboxyl-containing polyacrylate and/or polyester is prepared in an organic solvent, optionally crosslinking agents and also pigments and fillers are dispersed in the organic
15 solution, and the resulting dispersion, following neutralization of the carboxyl groups of the binder, is dispersed in water.

A disadvantage of this process is that the organic solvent has to be removed by an azeotropic
20 distillation after the aqueous dispersions have been prepared. This additional process step entails additional costs. Furthermore, this distillative removal of the solvent can be carried out only at the premises of the coating composition manufacturer, and
25 not at those of the customer. It is therefore necessary to transport and store the finished, aqueous coating materials, which leads frequently to problems, especially in the area of automotive refinishing, where very long shelf lives of at least 24 months are

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required.

The crosslinking agents used to prepare the coating compositions described in DE-B 25 07 884 are blocked polyisocyanates, epoxy resins and/or amino 5 resins. These coating compositions described therein therefore cure fully only at elevated temperatures of between 100 and 300 degrees C and are therefore unsuitable for the area of refinishing.

Finally, EP-A-368 499 discloses aqueous coating 10 compositions wherein the hydroxyl-containing binders are polyethers or polyesters containing ether groups and the crosslinking agents are amine/formaldehyde resins. These coating compositions are prepared by first of all preparing the binder and the crosslinking 15 agent in an organic solvent. Shortly before the application of the coating composition, a curing catalyst is added to this mixture and the formulation is adjusted with water to the desired viscosity.

These aqueous coating compositions known from EP-A- 20 368 499, however, have the disadvantage of a completely inadequate compatibility of the individual components of the coating composition. As a consequence they are unsuitable for the preparation of clearcoats. Furthermore, these coating compositions cure only at 25 elevated temperatures and are therefore unsuitable for the area of refinishing. A final, further disadvantage is the inadequate weathering stability of the resulting coatings.

The object of providing an aqueous coating

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composition which has improved properties and/or provides improved coating films in relation to the aqueous two-component polyurethane coating compositions known from EP-B-358 979 is largely achieved by the as yet unpublished German Patent Application P 44 21 823.0. P 44 21 823.0 describes coating compositions consisting of at least three components, which compositions are characterized in that the component (I) contains as binder at least one acrylate copolymer which is dissolved or dispersed in organic solvent and has a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 40 to 200 and an acid number of from 5 to 150 and/or a polyurethane resin having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 20 to 200 and an acid number of from 5 to 150 and, if desired, a further binder, the binder components being selected such that a 50% strength solution of the binder in ethoxyethyl propionate has a viscosity of not more than 2.5 dPas at 23 degrees C,

in that the component (II) contains at least one nonblocked polyisocyanate as crosslinking agent, and in that the component (III) is essentially binder-free and contains water.

Coatings prepared from coating compositions in accordance with P 44 21 823.0 exhibit, in comparison to aqueous coating compositions based on aqueous acrylate copolymer dispersions, improved leveling, improved gloss, improved relaxation (low graininess), lower

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boil-mark tendency, improved spray safety, improved fullness and an improved weathering resistance. Moreover, such coating compositions are suitable for the area of automotive refinishing; in other words,
5 they can be fully cured at low temperatures (in general < 80 degrees C) and lead to coatings which go a long way toward meeting the requirements commonly placed on an automotive refinish.

Nevertheless, even when the 3-component systems
10 in accordance with the as yet unpublished German Patent Application P 44 21 823.0 are employed as automotive refinishes, there are still problems on the fully cured coatings as a result of boil marks, gray haze and/or textured surfaces, caused by poor leveling of the
15 coating compositions.

Problem and solution

Therefore, the object set is to provide coating systems for automotive refinishing which leads [sic],
20 under the conditions of automotive refinishing, to coatings which exhibit no surface problems, such as boil marks or textures, and no impairment of the optical quality, such as gray haze.

This object has surprisingly been achieved by
25 the coating composition of the type specified at the outset, which is characterized in that

1.) Component (I) contains as binder (A)

(A1) at least one acrylate copolymer (A1) which is

dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight M_n of between 1000 and 30,000 daltons, an OH number of from 40 to 200 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or

- 10 (A2) at least one polyester resin (A2) which is dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 30 to 250 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or

15 (A3) at least one polyurethane resin (A3) which is dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 20 to 200 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and

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(A4) if desired, at least one further binder,

the binders (A1), (A2), (A3) and, optionally, (A4)
being selected such that a 50% strength solution
5 of the binder (A) in ethoxyethyl propionate has a
viscosity of <= 6.0 dPa.s at 23°C,

2.) component (II) comprises as crosslinking agent (F)
at least one di- and/or polyisocyanate (F1) which
10 is optionally dissolved or dispersed in one or
more organic solvents, and, optionally, at least
one further crosslinking agent consisting of at
least one epoxide compound (F2) having at least
two epoxide groups per molecule and, optionally,
15 at least one amino resin (F3), and

3.) component (III) comprises components (A1) and/or
(A2) and/or (A3) and/or (A4) in aqueous
dispersion.

20 The present invention additionally relates to a process for preparing these coating compositions and the use of the coating compositions in refinishing, for the coating of plastics and as topcoat or filler.

25 It is surprising that the novel coating compositions possess better properties than aqueous coating compositions which comprise the same binders and crosslinking agents but in which the binders, in accordance with the teaching of EP-B-358 979, have been

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incorporated into the coating composition in the form of an aqueous dispersion and not as an organic solution or dispersion. Or, alternatively, in accordance with the teaching of the as yet unpublished German Patent 5 Application P 44 21 823.0, the binders and the polyisocyanate crosslinking agents have been incorporated as an organic solution into the essentially binder-free component (III).

Thus, in comparison to these coating compositions, 10 the novel coating compositions are distinguished by improved gloss, good fullness, lower boil-mark tendency, by improved spray safety and by improved leveling, and good weathering resistance.

It is also surprising that the novel coating 15 compositions can be prepared from the at least three components by simple mixing without the necessity of complex apparatus for mixing and/or dispersing. The novel coating compositions are therefore particularly suitable for the area of automotive refinishing, since 20 the coating compositions can be prepared by the coater, directly prior to application of the coating compositions, by simple mixing of the components and can be cured fully at low temperatures.

A further advantage is that the aqueous coating 25 compositions prepared from the at least three components have only a low content of volatile organic solvents (VOC = Volatile Organic Content <= 3.2, preferably <= 2.8, pounds per gallon), although the coating compositions are prepared with the use of

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crosslinking agents and binders dissolved or dispersed in organic solvents.

Moreover, the novel coating compositions insure a high degree of variability, since it is possible not only to
5 employ crosslinking agents, pigments and additives recommended for aqueous coating compositions but also crosslinking agents, pigments and additives which are employed in conventional systems.

Finally, the novel components of the coating
10 compositions are notable for a very good shelf life, which corresponds to that of conventional coating compositions.

Implementation of the invention

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Components (I), (II), (III) and (IV) of the novel coating composition

In the text below, the individual components (I), (II), (III) and (IV) of the novel coating
20 composition will first of all be described in more detail.

Component (I)

It is essential to the invention that component
25 (I) of the novel coating composition contains, as binder (A)

(A1) at least one acrylate copolymer (A1) which is dissolved or dispersed in one or more organic,

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optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight 5 Mn of between 1000 and 30,000 daltons, an OH number of from 40 to 200 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or
(A2) at least one polyester resin (A2) which is dissolved or dispersed in one or more organic, 10 optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH 15 number of from 30 to 250 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or
(A3) at least one polyurethane resin (A3) which is dissolved or dispersed in one or more organic, 20 optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 20 to 200 mg of KOH/g and an acid 25 number of from 5 to 150 mg of KOH/g, and
(A4) if desired, a further binder.

In this context, the binders (A1), (A2), (A3) and, optionally, (A4) are selected such that a 50%

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strength solution of the binder (A) in ethoxyethyl propionate has a viscosity of less than or equal to 6.0 dPa.s at 23 degrees C.

As acrylate copolymer (A1) containing hydroxyl groups and acid groups, all acrylate copolymers having the indicated OH numbers, acid numbers and molecular weights are suitable. It is preferred to employ acrylate copolymers which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of

10 <= 6.0 dPa.s at 23 degrees C.

As component (A1) it is also preferred to employ acrylate copolymers which are obtainable by polymerization in an organic solvent or a solvent mixture, and in the presence of at least one polymerization initiator, of

- a1) an acid-group-free (meth)acrylic ester which is different from (a2), (a3), (a4), (a5), and (a6) and is copolymerizable with (a2), (a3), (a4), (a5), and (a6), or a mixture of such monomers,
- 20 a2) an ethylenically unsaturated monomer which carries at least one hydroxyl group per molecule and is free from acid groups, which is copolymerizable with (a1), (a3), (a4), (a5), and (a6) and is different from (a5), or a mixture of such monomers,
- 25 a3) an ethylenically unsaturated monomer which carries at least one acid group which can be converted into the corresponding acid anion group per

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molecule and is copolymerizable with (a1), (a2), (a4), (a5), and (a6), or a mixture of such monomers, and

- (a4) if desired, one or more vinyl esters of α -branched
5 monocarboxylic acids having 5 to 18 carbon atoms per molecule, and/or
a5) if desired, at least one reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of an α -branched monocarboxylic
10 acid having 5 to 18 carbon atoms per molecule or, instead of the reaction product, an equivalent quantity of acrylic and/or methacrylic acid, which is then reacted, during or after the polymerization reaction with the glycidyl ester of an α -branched monocarboxylic acid having 5 to 18
15 carbon atoms per molecule,
a6) if desired, an acid-group-free, ethylenically unsaturated monomer which is copolymerizable with (a1), (a2), (a3), (a4), and (a5) and is different from (a1), (a2), (a4) and (a5), or a mixture of such monomers,

(a1), (a2), (a3), (a4), (a5), and (a6) being selected in nature and quantity such that the polyacrylate resin
25 (A1) has the desired OH number, acid number and the desired molecular weight.

In order to prepare the polyacrylate resins employed in accordance with the invention it is possible to employ as component (a1) any acid-group-

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free ester of (meth)acrylic acid which is copolymerizable with (a2), (a3), (a4), (a5) and (a6), or a mixture of such (meth)acrylic esters. Examples are alkyl acrylates and alkyl methacrylates having up to 20
5 carbon atoms in the alkyl radical, for example methyl, ethyl, propyl, butyl, hexyl, ethylhexyl, stearyl and lauryl acrylate and methacrylate, and cycloaliphatic (meth)acrylic esters, for example cyclohexyl (meth)-acrylate, isobornyl (meth)acrylate, dicyclopentaene
10 [sic] (meth)acrylate and tert-butyldicyclohexyl (meth)-acrylate.

As component (a1) it is also possible to employ ethyltriglycol (meth)acrylate and methoxyoligoglycol (meth)acrylate having a number-average molecular weight
15 Mn of preferably 550 daltons or other ethoxylated and/or propoxylated, hydroxyl-free (meth)acrylic acid derivatives.

As component (a2) it is possible to employ ethylenically unsaturated monomers which carry at least
20 one hydroxyl group per molecule and are free from acid groups, and which are copolymerizable with (a1), (a2) [sic], (a3), (a4), (a5) and (a6) and are different from (a5), or a mixture of such monomers. Examples are hydroxyalkyl esters of acrylic acid, methacrylic acid
25 or of another alpha,beta-ethylenically unsaturated carboxylic acid. These esters may be derived from an alkylene glycol which is esterified with the acid, or they may be obtained by reacting the acid with an alkylene oxide. As component (a2) it is preferred to

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employ hydroxyalkyl esters of acrylic acid or methacrylic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, reaction products of cyclic esters, for example epsilon-caprolactone and 5 these hydroxyalkyl esters, or mixtures of these hydroxyalkyl esters and/or epsilon-caprolactone-modified hydroxyalkyl esters.

Examples of such hydroxyalkyl esters are 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 10 3-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, hydroxystearyl acrylate and hydroxystearyl methacrylate. Corresponding esters of other unsaturated acids, for example ethacrylic acid, crotonic acid and similar acids having up to about 6 carbon atoms per molecule, can also be employed. 15

In addition, it is also possible to employ as component (a2) olefinically unsaturated polyols. Preferred poly-20 acrylate resins (A) are obtained if trimethylolpropane monoallyl ether is employed, at least in part, as component (a2). The proportion of trimethylolpropane monoallyl ether is customarily from 2 to 10% by weight, based on the overall weight of the monomers (a1) to 25 (a6) which are employed to prepare the polyacrylate resin. In addition, however, it is also possible to add from 2 to 10% by weight, based on the overall weight of the monomers which are employed to prepare the polyacrylate resin, of trimethylolpropane monoallyl

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ether to the finished polyacrylate resin. The olefinically unsaturated polyols, such as trimethylolpropane monoallyl ether in particular, may be employed as sole hydroxyl-containing monomers, but, in 5 particular, proportionally in combination with others of the hydroxyl-containing monomers mentioned.

As component (a3) it is possible to employ any ethylenically unsaturated monomer which carries at least one acid group, preferably a carboxyl group, per 10 molecule and is copolymerizable with (a1), (a2), (a4), (a5) and (a6), or a mixture of such monomers. As component (a3) it is particularly preferred to employ acrylic acid and/or methacrylic acid. However, it is also possible to employ other ethylenically unsaturated 15 carboxylic acids having up to 6 carbon atoms in the molecule. Examples of such acids are ethacrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid. It is also possible to employ as component (a3) for example, ethylenically unsaturated sulfonic or 20 phosphonic acids, and/or their partial esters. As component (a3) it is possible in addition to employ mono(meth)acryloyloxyethyl maleate, mono(meth)acryloyloxyethyl succinate and mono(meth)acryloyloxyethyl phthalate.

25 As component (a4), one or more vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule are employed. The branched monocarboxylic acids can be obtained by reacting formic acid or carbon monoxide and water with olefins in the

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presence of a liquid, strongly acidic catalyst; the olefins may be products of the cracking of paraffinic hydrocarbons, such as mineral oil fractions, and may contain both branched and straight-chain acyclic and/or 5 cycloaliphatic olefins. The reaction of such olefins with formic acid or with carbon monoxide and water produces a mixture of carboxylic acids in which the carboxyl groups are located predominantly on a quaternary carbon atom. Examples of other olefinic 10 starting materials are propylene trimer, propylene tetramer and diisobutylene. However, the vinyl esters can also be prepared in a manner known per se from the acids, for example by reacting the acid with acetylene. It is particularly preferred - owing to their ready 15 availability - to employ vinyl esters of saturated aliphatic monocarboxylic acids, having 9 to 11 carbon atoms, which are branched at the alpha carbon atom.

As component (a5), the reaction product of acrylic acid and/or methacrylic acid with the glycidyl 20 ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule is employed. Glycidyl esters of highly branched monocarboxylic acids are obtainable under the trade name "Cardura". The reaction of the acrylic or methacrylic acid with the glycidyl 25 ester of a carboxylic acid having a tertiary alpha carbon atom can be carried out beforehand, during or after the polymerization reaction. As component (a5) it is preferred to employ the reaction product of acrylic and/or methacrylic acid with the glycidyl ester of

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Versatic acid. This glycidyl ester is obtainable commercially under the name "Cardura E10".

As component (a6) it is possible to employ all ethylenically unsaturated monomers which are free from 5 acid groups, are copolymerizable with (a1), (a2), (a3), (a4) and (a5) and are different from (a1), (a2), (a3) and (a4) or mixtures of such monomers. It is preferred to employ as component (a6) vinyl-aromatic hydrocarbons, such as styrene, alpha-alkylstyrenes and 10 vinyltoluene.

As component (a6) it is also possible to employ, in combination with other monomers mentioned as being suitable as component (a6), polysiloxane macromonomers. Suitable polysiloxane macromonomers are 15 those having a number-average molecular weight Mn of from 1000 to 40,000 daltons, preferably from 2000 to 10,000 daltons, and on average from 0.5 to 2.5, preferably from 0.5 to 1.5, ethylenically unsaturated double bonds per molecule. Examples of suitable 20 polysiloxane macromonomers are those described in DE-A 38 07 571 on pages 5 to 7, those in DE-A 37 06 095 in columns 3 to 7, those in EP-B 358 153 on pages 3 to 6 and those in US-A 4,754,014 in columns 5 to 9. Also suitable are other acryloxsilane-containing vinyl 25 monomers having the abovementioned molecular weights and contents of ethylenically unsaturated double bonds, examples being compounds which can be prepared by reacting hydroxy-functional silanes with epichlorohydrin and then reacting the reaction product with

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methacrylic acid and/or hydroxyalkyl esters of (meth)acrylic acid.

It is preferred as component (a6) to employ the polysiloxane macromonomers detailed in the as yet 5 unpublished German Patent Application P 44 21 823.0.

Other examples of polysiloxane macromonomers which are suitable as component (a6) are the compounds mentioned in the international patent application having the publication number WO 92/22615 on page 12, 10 line 18, to page 18, line 10.

The quantity of the polysiloxane macromonomer(s) (a6) employed to modify the acrylate copolymers (A1) is than 5% by weight, preferably from 0.5 to 2.5% by weight, and with particular preference 15 from 0.05 to 0.8% by weight, based in each case on the overall weight of the monomers which are employed to prepare the copolymer (A1).

The use of such polysiloxane macromonomers leads to an improvement in the slip of the novel 20 aqueous coating compositions.

The nature and quantity of components (a1) to (a6) is [sic] selected such that the polyacrylate resin (A1) has the desired OH number, acid number and glass transition temperature. Acrylate resins employed with 25 particular preference are obtained by the polymerization of

(a1) from 20 to 60% by weight, preferably from 30 to 50% by weight, of component (a1),

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- (a2) from 10 to 40% by weight, preferably from 15 to 35% by weight, of component (a2),
- (a3) from 1 to 15% by weight, preferably from 2 to 8% by weight, of component (a3),
- 5 (a4) from 0 to 25% by weight, preferably from 5 to 15% by weight, of component (a4),
- (a5) from 0 to 25% by weight, preferably from 5 to 15% by weight, of component (a5) and
- 10 (a6) from 5 to 30% by weight, preferably from 10 to 20% by weight, of component (a6),

the sum of the proportions by weight of components (a1) to (a6) being in each case 100% by weight.

The preparation of the polyacrylate resins (A1)
15 employed in accordance with the invention is carried out in an organic solvent or solvent mixture and in the presence of at least one polymerization initiator. The organic solvents and polymerization initiators employed are those solvents and polymerization initiators which
20 are customary for the preparation of polyacrylate resins and are suitable for the preparation of aqueous dispersions. In this context, the solvents may participate in the reaction with the crosslinking component (II) and thus act as reactive diluents.
25 Examples of solvents which can be used are butylglycol, 2-methoxypropanol, n-butanol, methoxybutanol, n-propanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene

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glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, triethylol-propane, ethyl 2-hydroxypropionate and 3-methyl-3-methoxybutanol, and also derivatives based on propylene glycol, for example ethyl ethoxypropionate, isopropoxypropanol, methoxypropyl acetate and the like. In this context it is also possible to prepare the polyacrylate resins (A1) first of all in a solvent which is not water-dilutable and to replace this solvent, after the polymerization, partially if desired, by water-dilutable solvent.

Examples of polymerization initiators which can be used are initiators which form free radicals, for example tert-butyl peroxyethylhexanoate, benzoyl peroxide, azobisisobutyronitrile and tert-butyl perbenzoate. The initiators are preferably employed in a quantity of from 2 to 25% by weight, particularly preferably from 4 to 10% by weight, based on the overall weight of the monomers.

The polymerization is expediently carried out at a temperature of from 80 to 160 degrees C, preferably from 110 to 160 degrees C. The solvents employed are preferably ethoxyethyl propionate and isopropoxypropanol.

The polyacrylate resin (A1) is preferably prepared by a two-stage process, since in this way the resulting aqueous coating compositions have better processability. It is preferred, therefore, to employ polyacrylate resins which are obtainable by

1. polymerizing a mixture of (a1), (a2), (a4), (a5) and (a6) or a mixture of portions of components (a1), (a2), (a4), (a5) and (a6) in an organic solvent,
2. after at least 60% by weight of the mixture consisting of (a1), (a2), (a4), (a5) and, if appropriate, (a6) has been added, adding (a3) and the remainder, if appropriate, of components (a1), (a2), (a4), (a5) and (a6), and continuing polymerization, and
3. after the end of the polymerization, if desired, at least partially neutralizing the resulting polyacrylate resin, i.e. converting the acid groups into the corresponding acid anion groups.

In addition, however, it is also possible initially to charge components (a4) and/or (a5) together with at least one portion of the solvent and to meter in the remaining components. Furthermore, it is also possible to include in the initial charge only portions of components (a4) and/or (a5) together with at least one portion of the solvent, and to add the remainder of these components as described above. It is preferred, for example, initially to charge at least 20% by weight of the solvent and about 10% by weight of component (a4) and (a5) and, if appropriate, portions of components (a1) and (a6).

Also preferred is the preparation of the polyacrylate

resins (a1) which are employed in accordance with the invention by a two-stage process in which stage (I) lasts from 1 to 8 hours, preferably from 1.5 to 4 hours, and the addition of the mixture of (a3) and any 5 remaining amount of components (a1), (a2), (a4), (a5) and (a6) is made over a period of from 20 to 120 minutes, preferably over a period of from 30 to 90 minutes. When the addition of the mixture of (a3) and any remaining amount of components (a1), (a2), (a4), 10 (a5) and (a6) is complete, polymerization is continued until all the monomers employed have undergone essentially complete reaction.

The quantity and rate of addition of the initiator is [sic] preferably chosen such that a 15 polyacrylate resin (A1) having a number-average molecular weight Mn of from 1000 to 30,000 daltons is obtained. It is preferred to commence the addition of initiator at some time, in general about 15 minutes, before adding the monomers. A further preferred 20 procedure is one in which the addition of the initiator is commenced at the same time as the addition of the monomers and is terminated about half an hour after the addition of the monomers has been ended. The initiator is preferably added in a constant quantity per unit 25 time. When the addition of initiator has ended, the reaction mixture is maintained at polymerization temperature for a time (generally 1.5 hours) sufficient for all the monomers employed to have undergone essentially complete reaction. "Essentially complete

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reaction" is intended to denote that, preferably, 100% by weight of the monomers employed has been reacted, but that it is also possible for a small proportion of residual monomer, of no more than up to about 0.5% by 5 weight, based on the weight of the reaction mixture, possibly to remain unreacted.

For the preparation of the polyacrylate resins (A1), the monomers are preferably polymerized at a polymerization solids content which is not too high, 10 preferably at a polymerization solids content of from 80 to 50% by weight, and then the solvents are removed partially by distillation, so that the polyacrylate resin solutions formed have a solids content of preferably from 80 to 60% by weight.

15 Suitable polyesters (A2) containing hydroxyl groups and acid groups which can be converted into the corresponding acid anion groups are all polyesters having the stated OH numbers, acid numbers and molecular figures. It is preferred to employ polyesters 20 which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of <= 6.0 dPa.s at 23 degrees C.

Preference is given to the employment, as component (A2), of polyesters which are obtainable by 25 reaction of

- p1) polycarboxylic acids or esterifiable derivatives thereof, together if desired with monocarboxylic acids,

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- p2) polyols, together if desired with monoools,
- p3) if desired, further modifying components, and
- p4) if desired, a component which is reactive with the reaction product of (p1), (p2) and, if used, (p3).

5

Examples of polycarboxylic acids which can be employed as component (p1) are aromatic, aliphatic and cycloaliphatic polycarboxylic acids. As component (p1) it is preferred to employ aromatic and/or aliphatic 10 polycarboxylic acids.

Examples of suitable polycarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, halophthalic acids, such as tetrachloro- and tetra- bromophthalic acid, adipic acid, glutaric acid, azelaic 15 acid, sebacic acid, fumaric acid, maleic acid, trimellitic acid, pyromellitic acid, tetrahydraphthalic acid, hexahydraphthalic acid, 1,2-cyclo- hexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 4-methylhexa- 20 hydrophthalic acid, endomethylenetetrahydraphthalic acid, tricyclodecanedicarboxylic acid, endoethylene- hexahydraphthalic acid, camphoric acid, cyclohexane- tetracarboxylic acid, cyclobutanetetracarboxylic acid and others. The cycloaliphatic polycarboxylic acids can 25 be employed both in their cis and in their trans form and as a mixture of their two forms. Also suitable are the esterifiable derivatives of the abovementioned polycarboxylic acids, for example their mono- or polyesters with aliphatic alcohols having 1 to 4 carbon

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atoms or hydroxy alcohols having 1 to 4 carbon atoms. Furthermore, it is also possible to employ the anhydrides of the abovementioned acids, where they exist.

5 It is also possible, if desired, to employ together with the polycarboxylic acids, monocarboxylic acids, examples being benzoic acid, tert-butylbenzoic acid, lauric acid, isononanoic acid and fatty acids of naturally occurring oils. Isononanoic acid is
10 preferably employed as monocarboxylic acid.

Suitable alcohol components (p2) for preparing the polyester (A2) are polyhydric alcohols, such as ethylene glycol, propanediols, butanediols, hexanediols, neopentyl hydroxypivalate, neopentyl
15 glycol, diethylene glycol, cyclohexanediol, cyclohexanedimethanol, trimethylpentanediol, ethylbutylpropanediol, ditrimethylolpropane, trimethylolethane, trimethylolpropane, glycerol, pentaerithritol, dipentaerithritol, trishydroxyethyl isocyanate, polyethylene
20 glycol, polypropylene glycol, together if desired with monohydric alcohols, for example butanol, octanol, lauryl alcohol, cyclohexanol, tert-butyl cyclohexanol, ethoxylated and/or propoxylated phenols.

Particularly suitable as component (p3) for the
25 preparation of the polyesters (A2) are compounds which have a group which is reactive toward the functional groups of the polyester, with the exception of the compounds mentioned as component (p4). As modifying component (p3) it is preferred to use polyisocyanates

and/or diepoxide compounds, and also, if desired, monoisocyanates and/or monoepoxide compounds. Examples of suitable components (p3) are described in DE-A-40 24 204 on page 4, lines 4 to 9.

5 As component (p4) for the preparation of the polyesters (A2), suitable compounds are those having, in addition to a group which is reactive toward the functional groups of the polyester (A2), a tertiary amino group as well, examples being monoisocyanates
10 having at least one tertiary amino group or mercapto compounds having at least one tertiary amino group. For details, reference is made to DE-A-40 24 204, page 4, lines 10 to 49.

The polyesters (A2) are prepared by the known
15 methods of esterification, as is described, for example, in DE-A-40 24 204, page 4, lines 50 to 65.

In this case the reaction is usually carried out at temperatures of between 180 and 280 degrees C, if desired in the presence of a suitable esterification
20 catalyst such as, for example, lithium octoate, dibutyltin oxide, dibutyltin dilaurate, para-toluene-sulfonic acid and the like.

The preparation of the polyesters (A2) is customarily carried out in the presence of small
25 quantities of a suitable solvent as entraining agent. Examples of entraining agents which are employed are aromatic hydrocarbons such as, in particular, xylene, and (cyclo)aliphatic hydrocarbons, for example cyclohexane.

It is particularly preferred to employ as component (A2) polyesters which have been prepared by a two-stage process, involving first of all preparing a hydroxyl-containing polyester having an OH number of 5 from 100 to 300 mg of KOH/g, an acid number of less than 10 mg of KOH/g and a number-average molecular weight Mn of from 500 to 2000 daltons, which in a second stage is then reacted with carboxylic anhydrides to give the desired polyester (A2). In this context, 10 the quantity of carboxylic anhydrides is selected such that the resulting polyester has the desired acid number. Suitable anhydrides for this reaction are all acid anhydrides which are customarily employed, for example hexahydrophthalic anhydride, trimellitic 15 anhydride, pyromellitic anhydride, phthalic anhydride, camphoric anhydride, tetrahydrophthalic anhydride, succinic anhydride and mixtures of these and/or other anhydrides and, in particular, anhydrides [sic] of aromatic polycarboxylic acids, such as trimellitic 20 anhydride.

It is possible, if desired, for the polyacrylate resin (A1) to have been prepared at least partially in the presence of the polyester (A2). In this case it is advantageous to prepare at least 20% by 25 weight and, with particular advantage, from 40 to 80% by weight of component (A1) in the presence of component (A2).

Any remaining amount of component (A1) is subsequently added to the binder solution. In this case it is

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possible for this already polymerized resin to have the same monomer composition as the polyacrylate resin synthesized in the presence of the polyester. However, it is also possible to add a hydroxyl-containing 5 polyacrylate resin having a different monomer composition. In addition, it is possible to add a mixture of different polyacrylate resins and/or polyesters, in which case, if desired, one resin has the same monomer composition as the polyacrylate resin 10 synthesized in the presence of the polyester.

Suitable hydroxyl- and acid-group-containing polyurethane resins (A3) are all polyurethane resins having the stated OH numbers, acid numbers and molecular figures. It is preferred to employ poly- 15 urethane resins which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of <= 6.0 dPa.s at 23 degrees C.

Examples of suitable polyurethane resins are described in the following documents: EP-A-355 433, 20 DE-A-35 45 618, DE-A-38 13 866, DE-A-32 10 051, DE-A- 26 24 442, DE-A-37 39 332, US-A-4,719,132, EP-A-89 497, US-A-4,558,090, US-A-4,489,135, DE-A-36 28 124, EP-A- 158 099, DE-A-29 26 584, EP-A-195 931, DE-A-33 21 180 and DE-A-40 05 961.

25 In component (I) it is preferred to employ polyurethane resins which can be prepared by reacting isocyanate-group-containing prepolymers with compounds which are reactive toward isocyanate groups.

The preparation of prepolymers containing

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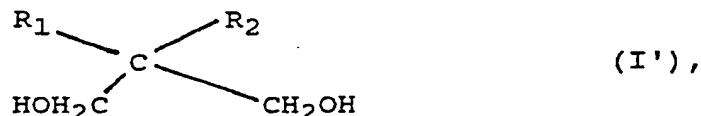
- isocyanate groups can be carried out by reaction of polyols having a hydroxyl number of from 10 to 1800, preferably from 50 to 1200 mg of KOH/g with excess polyisocyanates at temperatures of up to 150 degrees C,
5 preferably from 50 to 130 degrees C, in organic solvents which are not able to react with isocyanates. The ratio of equivalents of NCO to OH groups is between 2.0:1.0 and > 1.0:1.0, preferably between 1.4:1 and 1.1:1.
- 10 The polyols employed for the preparation of the prepolymer may be of low molecular weight and/or high molecular weight and may contain slow-to-react anionic groups or groups capable of forming anions. It is also possible to use low molecular weight polyols having a
15 molecular weight of from 60 up to 400 daltons in order to prepare the prepolymers which contain isocyanate groups. In this case, quantities of up to 30% by weight of the overall polyol components, preferably from about 2 to 20% by weight, are employed.
- 20 In order to obtain an NCO prepolymer of high flexibility, a high proportion of a predominantly linear polyol should be added, having a preferred OH number of from 30 to 150 mg of KOH/g. Up to 97% by weight of the overall polyol may be composed of saturated and
25 unsaturated polyesters and/or polyethers having a number-average molecular weight Mn of from 400 to 5000 daltons. The polyetherdiols selected should not introduce any excessive quantities of ether groups, since otherwise the polymers formed swell in water.

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Polyesterdiols are prepared by esterification of organic dicarboxylic acids or anhydrides thereof with organic diols, or are derived from a hydroxycarboxylic acid or a lactone. In order to prepare branched 5 polyesterpolyols it is possible to employ, to a minor extent, polyols or polycarboxylic acids having a higher functionality.

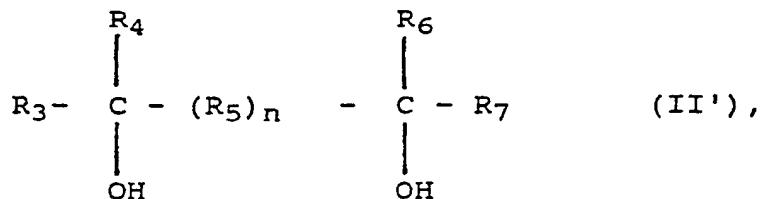
Preferably, the alcohol component employed for the preparation of the polyurethane resins consists, at 10 least in a certain proportion, of

a₁) at least one diol of the formula (I')



in which R₁ and R₂ are each an identical or 15 different radical and are an alkyl radical of 1 to 18 carbon atoms, an aryl radical or a cycloaliphatic radical, with the proviso that R₁ and/or R₂ may not be methyl, and/or

20 a₂) at least one diol of the formula (II')



in which R₃, R₄, R₆ and R₇ are each identical or different radicals and are an alkyl radical of 1 to 6 carbon atoms, a cycloalkyl radical or an aryl

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radical, and R₅ is an alkyl radical of 1 to 6 carbon atoms, an aryl radical or an unsaturated alkyl radical of 1 to 6 carbon atoms, and n is either 0 or 1.

5

As component (a₁), suitable propanediols of the formula (I') are all those in which either R₁ or R₂ or R₁ and R₂ is not methyl, examples being 2-butyl-2-ethyl-propane-1,3-diol, 2-butyl-2-methylpropane-1,3-diol, 10 2-phenyl-2-methylpropane-1,3-diol, 2-propyl-2-ethylpropane-1,3-diol, 2-di-tert-butylpropane-1,3-diol, 2-butyl-2-propylpropane-1,3-diol, 1-dihydroxymethyl-bicyclo[2.2.1]heptane, 2,2-diethylpropane-1,3-diol, 2,2-dipropylpropane-1,3-diol, 2-cyclohexyl-2-methyl-15 propane-1,3-diol and others.

As component (a₂) (formula II')) it is possible to employ, for example, 2,5-dimethylhexane-2,5-diol, 2,5-diethylhexane-2,5-diol, 2-ethyl-5-methylhexane-2,5-diol, 2,4-dimethylpentane-2,4-diol, 2,3-dimethylbutane-20 2,3-diol, 1,4-(2'-hydroxypropyl)-benzene [sic] and 1,3-(2'-hydroxypropyl)-benzene [sic].

It is preferred to employ, as component (a₁), 2-propyl-2-ethylpropane-1,3-diol, 2,2-diethylpropane-1,3-diol, 2-butyl-2-ethylpropane-1,3-diol and 2-phenyl-25 2-ethylpropane-1,3-diol and, as component (a₂), 2,3-dimethylbutane-2,3-diol and also 2,5-dimethylhexane-2,5-diol. It is particularly preferred to employ, as component (a₁), 2-butyl-2-ethylpropane-1,3-diol and also 2-phenyl-2-ethylpropane-1,3-diol and, as component (a₂),

2,5-dimethylhexane-2,5-diol.

The components (a_1) and/or (a_2) are customarily employed in a quantity of from 0.5 to 15% by weight, preferably from 1 to 7% by weight, based in each case 5 on the overall weight of the structural components employed for the preparation of the polyurethane resins (A3).

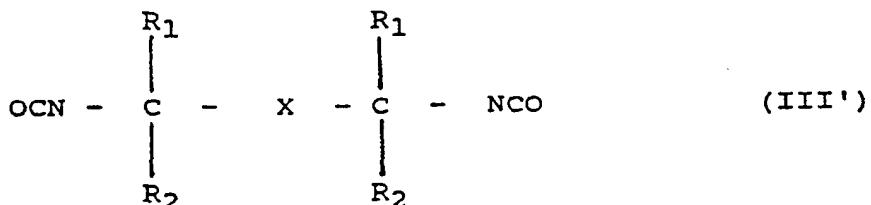
As typical multifunctional isocyanates for the preparation of the polyurethane resins, use is made of 10 aliphatic, cycloaliphatic and/or aromatic polyisocyanates having at least two isocyanate groups per molecule. The isomers or isomer mixtures of organic diisocyanates are preferred. Owing to their good resistance to ultraviolet light, (cyclo)aliphatic 15 diisocyanates give rise to products having a low tendency toward yellowing. The polyisocyanate component used to form the prepolymer may also contain a proportion of more highly functional polyisocyanates, provided this does not cause any gelling. Triisocyanates which have proven suitable are products formed 20 by trimerization or oligomerization of diisocyanates or by reaction of diisocyanates with polyfunctional OH- or NH-containing compounds. The mean functionality can be lowered, if desired, by adding monoisocyanates.

25 Examples of polyisocyanates which can be employed are phenylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, bisphenylene diisocyanate, naphthylene diisocyanate, diphenylmethane diisocyanate, isophorone diisocyanate, cyclobutane

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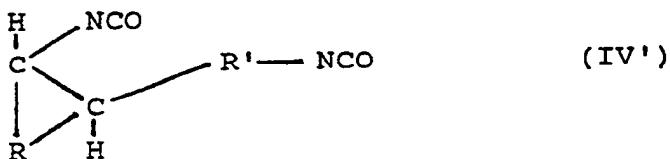
diisocyanate cyclopentylene diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, di-cyclohexylmethane diisocyanate, ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 5 pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethyl ethylene diisocyanate and trimethylhexane diisocyanate.

For the preparation of high-solids polyurethane resin solutions, use is made in particular of diisocyanates of the general formula (III')



in which X is a divalent, aromatic hydrocarbon radical, preferably an optionally halogen-, methyl- or methoxy-substituted naphthylene, diphenylene or 1,2-, 1,3- or 15 1,4-phenylene radical, particularly preferably a 1,3-phenylene radical, and R₁ and R₂ are an alkyl radical of 1-4 carbon atoms, preferably a methyl radical. Diisocyanates of the formula (III') are known (their preparation is described, for example, in EP-A-101 832, 20 US-A-3,290,350, US-A-4,130,577 and US-A-4,439,616) and some are obtainable commercially (1,3-bis-(2-isocyanatoprop-2-yl)-benzene, for example, is sold by the American Cyanimid [sic] Company under the trade name TMXDI (META)®).

25 Further preferred polyisocyanate components are diisocyanates of the formula (IV'):



where: R is a divalent alkyl or aralkyl radical of 3 to 20 carbon atoms and
 R' is a divalent alkyl or aralkyl radical of 1 to 20 carbon atoms.

5

Polyurethanes are generally not compatible with water unless in the course of their synthesis specific constituents are incorporated and/or particular preparation steps are undertaken. Thus, for the preparation of the polyurethane resins, it is possible to use compounds which contain two H-active groups which are reactive with isocyanate groups, and at least one group which insures dispersibility in water. Suitable groups of this kind are nonionic groups (e.g. polyethers), anionic groups, mixtures of these two groups, or cationic groups.

It is thus possible to incorporate into the polyurethane resin an acid number which is sufficient for the neutralized product to give a stable dispersion in water. Compounds used for this purpose contain at least one group which is reactive toward isocyanate groups and at least one group which is capable of forming anions. Suitable groups which are reactive toward isocyanate groups are, in particular, hydroxyl groups and also primary and/or secondary amino groups.

25

Groups capable of forming anions are carboxyl, sulfonic acid and/or phosphonic acid groups. Preference is given to the use of alkanoic acids having two substituents on the alpha carbon atom. The substituent may be a 5 hydroxyl group, an alkyl group or an alkylol group. These polyols have at least one, generally from 1 to 3, carboxyl groups in the molecule. They have from two to about 25, preferably 3 to 10, carbon atoms. The carboxyl groups-contained [sic] polyol may make up from 10 3 to 100% by weight, preferably from 5 to 50% by weight, of the overall polyol constituent in the NCO prepolymer.

The quantity of ionizable carboxyl groups which is available in salt form owing to the neutralization 15 of the carboxyl groups is generally at least 0.4% by weight, preferably at least 0.7% by weight, based on the solids content. The upper limit is about 12% by weight. The quantity of dihydroxyalkanoic acids in the unneutralized prepolymer gives rise to an acid number 20 of at least 5 mg of KOH/g, preferably at least 10 mg of KOH/g. In the case of very low acid numbers, further measures are generally necessary in order to achieve dispersibility in water. The upper limit of the acid number is at 150 mg of KOH/g, preferably at 40 mg of 25 KOH/g, based on the solids content. The acid number is preferably within the range from 20 to 40 mg of KOH/g.

The isocyanate groups of the prepolymer which contains isocyanate groups are reacted with a modifying agent. This modifying agent is preferably added in a

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quantity such that chain extensions, and thus increases in molecular weight, occur. Preferred modifying agents employed are organic compounds containing hydroxyl and/or secondary and/or primary amino groups,
5 especially di-, tri- and/or more highly functional polyols. Examples of polyols which can be employed are trimethylolpropane, 1,3,4 butanetriol, glycerol, erythritol, mesoerythritol, arabitol, adonitol, etc. It is preferred to employ trimethylolpropane.

10 In order to prepare the polyurethane resin according to the invention it is preferred first of all to prepare an isocyanato-containing prepolymer from which the desired polyurethane resin is then prepared by further reaction, preferably chain extension. In
15 this context, the reaction of the components takes place in accordance with the well-known methods of organic chemistry (cf. e.g. Kunststoff-Handbuch [Plastics handbook], Volume 7: Polyurethanes, edited by Dr. Y. Oertel, Carl Hanser Verlag, Munich, Vienna
20 1983). Examples of the preparation of the prepolymers are described in DE-A 26 24 442 and in DE-A 32 10 051. The polyurethane resins can be prepared in accordance with the known techniques (e.g. acetone method).

The components are preferably reacted in
25 ethoxyethyl propionate (EEP) as solvent. In this case the quantity of ethoxyethyl propionate can be varied within wide limits and should be sufficient to form a prepolymer solution of appropriate viscosity. In general up to 70% by weight, preferably from 5 to 50%

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by weight and, with particular preference, less than 20% by weight of solvent is employed, based on the solids content. For example, the reaction can be carried out, with very particular preference, at a 5 solvent content of 10-15% by weight of EEP, based on the solids content.

The reaction of the components can be carried out, if desired, in the presence of a catalyst, such as organotin compounds and/or tertiary amines.

10 For the preparation of the prepolymers, the quantities of the components are chosen such that the ratio of equivalents of NCO to OH groups is between 2.0:1.0 and > 1.0:1.0, preferably between 1.4:1 and 1.1:1. The NCO prepolymer contains at least about 0.5% by weight of 15 isocyanate groups, preferably at least 1% by weight of NCO, based on the solids content. The upper limit is at about 15% by weight, preferably 10% by weight, particularly preferably at 5% by weight of NCO.

Suitable components (A4) are all water-dilutable binders which are compatible with the other constituents of component (I), examples being acrylicized polyurethane resins and/or polyester-acrylates.

Component (I) preferably comprises as binder 25 (A)

at least 20% by weight of (A1), from 0 to 30% by weight of (A2), from 0 to 80% by weight of (A3) and, optionally, from 0 to 10% by weight of (A4),

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the sum of the proportions by weight of components (A1) to (A4) being in each case 100% by weight, based on the binder (A).

As constituent (B), component (I) may contain
5 all pigments which are conventional in coatings, in proportions of from 0 to 60% by weight based on component I. It is possible here to employ both the pigments which are customary in aqueous coating compositions, which do not react with water and/or do
10 not dissolve in water, and the pigments which are customarily employed in conventional coating compositions. The pigments may consist of inorganic or organic compounds and may impart a special effect and/or color. The coating composition according to the
15 invention therefore insures, on the basis of this large number of suitable pigments, a universal scope for use of the coating compositions, and makes it possible to realize a large number of colors.

Special-effect pigments which can be employed are metal
20 flake pigments, such as commercial aluminum bronze, aluminum bronzes which have been chromated in accordance with DE-A-36 36 183, and commercial stainless-steel bronzes, and also nonmetallic special-effect pigments, for example pearlescent pigments and
25 interference pigments. Examples of suitable inorganic color-imparting pigments are titanium dioxide, iron oxides, Sicotrans yellow and carbon black. Examples of suitable organic color-imparting pigments are Indanthrene blue, Cromophthal red, Irgazine orange and

Heliogen green.

As constituent (C), component (I) comprises at least one organic, optionally water-dilutable solvent. Such solvents may also participate in the reaction with 5 the crosslinking component (II) and therefore act as reactive diluents.

Examples of suitable solvents are the compounds already mentioned in connection with the preparation of the polyacrylate resins (A1) (see above). Also suitable 10 are esters, ketones, keto esters, glycol ether esters and the like. Those employed preferably are esters, alcohols and glycol ethers, particularly preferably ethoxyethyl propionate and isopropoxypyropanol.

Furthermore, the solvents (C) may consist in part or in 15 whole of low molecular weight oligomeric compounds which may be reactive or else unreactive toward the crosslinking component (II).

As constituent (D), component (I) comprises, if desired, at least one neutralizing agent. Examples of 20 suitable neutralizing agents are ammonia, ammonium salts, for example ammonium carbonate or ammonium hydrogen carbonate, and also amines, for example trimethylamine, triethylamine, tributylamine, dimethyl-aniline, diethylaniline, triphenylamine, dimethyl-25 ethanamine, diethylethanamine, methyldiethanamine, triethanolamine and the like. Neutralization may take place in organic phase or in aqueous phase. The preferred neutralizing agent employed is dimethylethanamine.

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The quantity of neutralizing agent employed overall in the novel coating composition is chosen such that from 1 to 100 equivalents, preferably from 50 to 90 equivalents, of the acid groups of the binder (A) are 5 neutralized.

In this context, the neutralizing agent may be added to component (I) and/or (II) and/or (III) and/or (IV). Preferably, however, the neutralizing agent is added to component (III).

10 As constituent (E), component (I) may contain at least one rheology-controlling additive. Examples of rheology-controlling additives are: crosslinked polymeric microparticles, as are disclosed, for example, in EP-A-38 127, inorganic phyllosilicates, for 15 example aluminum-magnesium silicates, sodium-magnesium phyllosilicates and sodium-magnesium-fluorine-lithium phyllosilicates of the montmorillonite type, and also synthetic polymers having ionic and/or associative groups, such as polyvinyl alcohol, poly(meth)-acrylamide, poly(meth)acrylic acid, polyvinyl-pyrrolidone, styrene-maleic anhydride or ethylene-maleic anhydride copolymers and derivatives thereof, or else hydrophobically modified, ethoxylated urethanes or polyacrylates. Polyurethanes are preferably employed as 20 rheology-controlling additives.

25

Furthermore, component (I) may contain at least one further conventional paint additive. Examples of such additives are antifoams, dispersion auxiliaries, emulsifiers, and leveling auxiliaries.

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It is of course also possible for the additives mentioned to be added separately to the coating composition. In this case the additives are then referred to as component (IV).

5 For the preparation of the novel coating compositions it is preferred to employ components (I) which comprise

- (A) from 20 to 90% by weight, preferably from 35 to 10 80% by weight, of the binder (A),
- (B) from 0 to 60% by weight of at least one pigment and/or filler,
- (C) from 5 to 50% by weight, preferably from 10 to 40% by weight, of at least one organic, optionally 15 water-dilutable solvent, and
- (D) from 0 to 20% by weight, preferably from 0.1 to 10% by weight, of at least one neutralizing agent
- (E) from 0 to 20% by weight, preferably from 2 to 10% by weight, of at least one customary auxiliary 20 and/or additive,

the sum of the proportions by weight of components (A) to (E) being in each case 100% by weight.

25 **Component (II)**

It is essential to the invention that the coating component (II) contains, as crosslinking agent, at least one preferably nonblocked di- and/or polyisocyanate (F1) which is optionally dissolved or dispersed

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in one or more organic, optionally water-dilutable solvents, and, if desired, at least one further crosslinking agent selected from at least one epoxide compound (F2) having at least two epoxide groups per 5 molecule and/or at least one amino resin (F3).

The polyisocyanate component (F1) may comprise any desired organic polyisocyanates having free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic structures. Preference is 10 given to employing polyisocyanates having 2 to 5 isocyanate groups per molecule and having viscosities of from 100 to 2000 mPas (at 23°C). If desired, small quantities of organic solvent, preferably from 1 to 25% by weight based on pure polyisocyanate, may be added to 15 the polyisocyanates in order, thus, to improve the ease of incorporation of the isocyanate and, if desired, to reduce the viscosity of the polyisocyanate to a value within the abovementioned ranges. Examples of solvents suitable as additives for the polyisocyanates are 20 ethoxyethyl propionate, butyl acetate and the like.

Examples of suitable isocyanates are described, for example, in "Methoden der organischen Chemie" [Methods of organic chemistry], Houben-Weyl, Volume 14/2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, 25 page 61 to 70, and by W. Siefken, Liebigs Ann. Chem. 562, 75 to 136. Suitable examples are the isocyanates mentioned in the context of the description of the polyurethane resins (A3), and/or polyurethane prepolymers containing isocyanate groups, which can be

- 45 -

prepared by reacting polyols with an excess of polyisocyanates and which are preferably of low viscosity.

It is also possible to employ polyisocyanates
5 which contain isocyanurate groups and/or biuret groups and/or allophanate groups and/or urethane groups and/or urea groups and/or uretdione groups. Polyisocyanates containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols,
10 for example trimethylolpropane and glycerol.

It is preferred to employ aliphatic or cyclo-aliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate or dicyclohexylmethane 4,4'-diisocyanate or mixtures of these polyisocyanates. Very particular preference is given to the use of mixtures of polyisocyanates, containing uretdione and/or
15 isocyanurate groups and/or allophanate groups, which are based on hexamethylene diisocyanate, as are formed by catalytic oligomerization of hexamethylene diisocyanate using appropriate catalysts. The polyisocyanate component (F1) may otherwise also be
20 composed of any desired mixtures of the polyisocyanates specified by way of example.

In a further embodiment of the invention, the polyisocyanate component (F1) consists of a mixture of blocked di- and/or polyisocyanates and the already

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mentioned nonblocked di- and/or polyisocyanates. In this case the blocked di- and/or polyisocyanates preferably make up the smaller proportion by weight of the polyisocyanate component (F1). Examples which may 5 be mentioned of blocking agents for the di- and/or polyisocyanates already set out above are: aliphatic, cycloaliphatic or araliphatic monoalkohols, for example methyl, butyl, octyl and lauryl alcohol, cyclohexanol or phenylcarbinol, hydroxylamines, such as ethanol-10 amine, oximes, such as methyl ethyl ketone oxime, acetone oxime or cyclohexanone oxime, amines, such as dibutylamine or diisopropylamine, malonic diesters, ethyl acetoacetate and/or epsilon-caprolactam.

In the novel coating compositions, the polyisocyanate component (F1) is employed advantageously in a quantity of at least 70% by weight, particularly preferably in a quantity of from 80 to 100% by weight, based on the overall weight of the crosslinking agent (F).

20 Examples of suitable polyepoxides (F2) are all known aliphatic and/or cycloaliphatic and/or aromatic polyepoxides, based for example on bisphenol A or bisphenol F.

Examples of suitable components (F2) include the 25 polyepoxides which are obtainable commercially under the designations Epikote® from Shell, Denacol® from Nagase Chemicals Ltd., Japan, for example Denacol EX-411 (pentaerythritol polyglycidyl ether), Denacol EX-321 (trimethylolpropane polyglycidyl ether), Denacol

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EX-512 (polyglycerol polyglycidyl ether) and Denacol EX-521 (polyglycerol polyglycidyl ether).

In the novel coating compositions, the polyepoxide component (F2) is advantageously employed in a quantity 5 of from 0 to 30% by weight, particularly preferably in a quantity of from 2 to 20% by weight, based on the overall weight of the crosslinking agent (F).

Examples of suitable amino resins (F3) are imino-functional melamine resins such as the products 10 obtainable commercially under the name Cymel® 325 from Cyanamid and Luwipal® LR 8839 from BASF AG.

The amino resin (F3) is employed in the novel coating compositions advantageously in a quantity of from 0 to 30% by weight, particularly preferably in a quantity of 15 from 2 to 20% by weight, based on the overall weight of the crosslinking agent (F).

Constituents (G) and (H) of coating component (II) correspond to the constituents (C) and (E) of coating component (I).

20 In order to prepare the novel coating compositions, it is preferred to employ components (II) which comprise

(F) from 50 to 100% by weight, preferably from 60 to 25 90% by weight, of at least one crosslinking agent (F),

(G) from 0 to 50% by weight, preferably from 10 to 40% by weight, of at least one organic, optionally water-dilutable solvent, and

(H) from 0 to 20% by weight, preferably from 0 to 10% by weight, of at least one customary auxiliary and/or additive,

5 the sum of the proportions by weight of components (F) to (H) being in each case 100% by weight.

Components (III) and (IV)

Constituents (L) and (M) of coating component
10 (III) correspond to the constituents (D) and (E) of coating component (I).

In order to prepare the novel coating compositions, it is preferred to employ components (III) which comprise

15

(J) from 40 to 90% by weight, preferably from 50 to 85% by weight, of water,

(K) from 5 to 50% by weight, preferably from 10 to 45% by weight, of components (A1) and/or (A2) and/or
20 (A3) and/or (A4) of the binder (A) in water-dispersed form,

(L) from 0 to 20% by weight, preferably from 2 to 10% by weight, of at least one neutralizing agent, and

(M) from 0 to 20% by weight, preferably from 2 to 10%
25 by weight, of at least one customary auxiliary and/or additive,

the sum of the proportions by weight of components (J) to (M) being in each case 100% by weight.

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Component (III), consisting of the water-dispersed form of component (A) and therefore of the water-dispersed form of components (A1) and/or (A2) and/or (A3) and/or (A4), can on the one hand be
5 prepared by preparing the components in organic solvent, then neutralizing the carboxyl groups with the neutralizing agent and, finally, introducing the neutralized components into deionized water, or on the other hand by emulsion polymerization of the monomeric
10 building blocks of the components in water.

Components (A1) and/or (A2) and/or (A3) and/or (A4) are preferably first of all prepared in organic solvent, then neutralized and finally dispersed in water in neutralized form.

15 In the preparation of the water-dispersed form of the polyacrylate component (A1), the polymerization is carried out in organic solvent, preferably in a plurality of stages, with separate monomer and initiator feed streams. With very particular
20 preference, the polyacrylate resin is prepared by the two-stage process already described above, in which

1. a mixture of (a1), (a2), (a4), (a5) and (a6) or a mixture of portions of components (a1), (a2),
25 (a4), (a5) and (a6) is polymerized in an organic solvent,
2. after at least 60% by weight of the mixture consisting of (a1), (a2), (a4), (a5) and, if appropriate, (a6) has been added, (a3) and any

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remaining amount of components (a1), (a2), (a4),
(a5) and (a6) are added and polymerization is
continued, and

3. after the end of polymerization, the polyacrylate
5 resin (A1) obtained is optionally neutralized, at
least partially.

Examples of suitable neutralizing agents as
employed in step 3. are the ammonia, ammonium salts and
amines (constituent (D) of component (I)) already
10 described in connection with the preparation of
component (I), it being possible for neutralization to
be carried out in organic or in aqueous phase. The
quantity of neutralizing agent employed overall to
neutralize component (A1) is chosen such that from 1 to
15 100 equivalents, preferably from 50 to 90 equivalents,
of the acid groups of the binder (A1) are neutralized.

As component (A2) in component (III) it is
preferred to employ polyesters which have been prepared
by a two-stage process in which, first of all, a
20 hydroxyl-containing polyester is prepared having an OH
number of from 100 to 300 mg of KOH/g, an acid number
of less than 10 mg of KOH/g and a number-average
molecular weight Mn of from 500 to 2000 daltons, which
then in a second stage is reacted with carboxylic
25 anhydrides to form the desired polyester (A2). The
quantity of carboxylic anhydrides is in this case
chosen such that the polyester obtained has the desired
acid number. After the end of the reaction the
polyester (A2) is at least partially neutralized, again

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employing the neutralizing agents (constituent (D) of component (I)) already described in connection with the preparation of component (I), and it being possible to carry out the neutralization in organic or in aqueous 5 phase.

For the preparation of the polyurethane resins (A3) in component (III) it is preferred first of all to prepare a prepolymer which contains isocyanate groups, and from which the polyurethane resin (A3) is then 10 prepared by further reaction, preferably by chain extension.

After the end of the polymerization the polyurethane resin obtained is at least partially neutralized, again using suitable neutralizing agents, 15 for example, the ammonia, ammonium salts and amines (component (D) of component (I)) already described in connection with the preparation of component (I), it being possible to carry out the neutralization in organic or in aqueous phase.

Suitable components (A4) which may if desired be present in addition are all water-dilutable and/or water-dispersible binders which are compatible with the other constituents of component (III), examples being acrylicized polyurethane resins and/or polyester-acrylates. 25

The novel coating compositions

To prepare the coating compositions, components (I), (II) and (III) are preferably employed in

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quantities such that the ratio of equivalents of hydroxyl groups of components (A1) and/or (A2) and/or (A3) and/or (A4) of the binder (A) to the crosslinking groups of the crosslinking agent (F) is between 1:2 and 5 2:1, preferably between 1:1.2 and 1:1.5.

Moreover, the novel coating compositions preferably have an overall content of conventional paint additives of from 0 to 10% by weight, of organic solvents of from 5 to 25% by weight, preferably from 10 to 20% by 10 weight, of water of from 25 to 60% by weight, preferably from 30 to 50% by weight, of binders (A) of from 15 to 60% by weight, preferably from 20 to 50% by weight, of crosslinking agents (F) of from 5 to 30% by weight, preferably from 10 to 20% by weight, and of 15 pigments and/or fillers of from 0 to 50% by weight, preferably from 0 to 30% by weight, based in each case on the overall weight of the coating composition.

Component (I) is prepared by methods known to the person skilled in the art, by mixing and, if 20 desired, dispersing the individual constituents. Thus, for example, the incorporation of color-imparting pigments is conventionally carried out by grinding (dispersing) the respective pigments in one or more binders. The grinding of the pigments is carried out 25 with the aid of customary devices, for example bead mills and sand mills.

Components (II), (III) and, if appropriate, (IV) are likewise prepared by methods which are well known to the person skilled in the art, by mixing

and/or dispersing the individual constituents.

The novel coating compositions are prepared by the following mixing method from components (I), (II), (III) and, if appropriate, (IV):

5 In order to prepare the novel coating compositions, components (I) and (II) are first of all mixed, these components (I) and (II) preferably containing no neutralizing agent. Then, if desired, component (IV) is added to this mixture. One option is then to add the
10 mixture thus obtained to the component (III), containing neutralizing agent, and to disperse the resulting coating composition; alternatively, component (III) containing the neutralizing agent is then added to the mixture thus obtained.

15 Furthermore, the novel coating composition can be prepared, for example, in analogy to the procedure just described, but with the neutralizing agent not being present in component (III) but being added separately prior to the addition of component (III).

20 Furthermore, the novel coating composition can also be prepared by first of all adding the neutralizing agent to component (I). In place of this mixing it is of course also possible to employ a component (I) already containing the neutralizing
25 agent. The resulting component (I) is then mixed with component (II) and, if appropriate, with component (IV) (simultaneously or successive mixing with (II) and, if appropriate, (IV)), and the mixture thus obtained is then either added to component (III) or has component

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(III) added to it, and the coating composition thus obtained in each case is also homogenized by dispersing.

The novel coating compositions can be applied
5 by conventional application methods, for example spraying, knife coating, spreading or dipping, to any desired substrates, for example metal, wood, plastic or paper.

The novel coating compositions are customarily
10 cured at temperatures below 120 degrees C, preferably at temperatures of not more than 80 degrees C. In specific embodiments of the novel coating compositions it is also possible to employ higher curing temperatures.

15 The novel coating compositions are preferably employed for the production of topcoats. The novel coating compositions can be employed both in the production-line finishing and in the refinishing of automobile bodies. Preferably, however, they are
20 employed in the area of refinishing and in the coating of plastics parts.

The novel aqueous coating compositions can be employed as fillers and for producing single-layer top coats, and also as pigmented basecoats or as clearcoats.
25 in a process for the production of a multilayer finish (basecoat/clearcoat process).

The invention will now be illustrated in more detail on the basis of working examples. In these examples all parts and percentages are by weight unless

expressly stated otherwise.

Examples

5 **Example 1: Preparation and application of a clearcoat**

**Example 1.1: Preparation of a water-dilutable acrylate
resin (A1) for component (I)**

1000 g of ethyl ethoxypropionate are charged to
10 a 4 l steel vessel equipped with monomer feed,
initiator feed, thermometer, oil heating and reflux
condenser and are heated to 130 degrees C. A solution
of 89.4 g of tert-butyl peroxyethylhexanoate in 145.7 g
of ethoxyethyl propionate is then added at a rate such
15 that the addition is complete after 4.5 hours. 5
minutes after beginning the addition of the tert-butyl
peroxyethylhexanoate solution, the addition of the
monomer mixture of (a1), (a2) and (a6):

20 (a1): 285 g of n-butyl methacrylate
 229 g of methyl methacrylate
 640 g of lauryl methacrylate
 (Commercial product Methacrylester 13 from Röhm
 GmbH, Darmstadt),
25 (a2): 270 g of hydroxyethyl acrylate and
 (a6): 238 g of styrene

is also commenced, the overall feed time for the first
monomer feed being 4 hours.

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2.5 hours after the first monomer feed has been started, a second monomer feed is commenced which consists of a mixture of (a2), (a3) and 27 g of ethoxypropionate:

5

(a2): 112 g of hydroxyethyl acrylate and
(a3): 54 g of acrylic acid,

the overall feed time for the second monomer feed being
10 1.5 hours.

The mixture (a1), (a2), (a3) and (a6) is added at a rate such that the addition is complete after 4 hours. Following the completion of the addition of the tert-butyl peroxyethylhexanoate solution, the reaction
15 mixture is held at 120 degrees C for 2 h more. The reaction mixture is adjusted to a solids content of 79.2% by distillative removal of the organic solvent (for 1 hour at 130 degrees C under reduced pressure). The resulting acrylate resin has an OH number of 140 mg
20 of KOH/g of solid resin, an acid number of 31.1 mg of KOH/g of solid resin, a number-average molecular weight Mn of 3220 daltons and a weight-average molecular weight Mw of 7505 daltons. The viscosity of a 55% strength solution of the acrylate resin in ethoxyethyl
25 propionate is 4.4 dPa.s (23°C).

Example 1.2: Preparation of the dispersion of a polyolefin resin (A3) for component (III)

1.2.1. Preparation of the polyester precursor

5 1088 g of neopentylglycol hydroxypivalate,
120 g of phthalic anhydride, 1268 g of isophthalic
acid, 21 g of 2-butyl-2-ethylpropanediol, 489 g of
neopentylglycol and 113 g of xylene as entraining agent
are weighed into a 4 l steel reactor which is suitable
10 for the polycondensation reactions.

The mixture is subsequently heated and the
water of condensation is removed continuously to an
acid number of < 3.5. The batch was cooled to about
100°C and adjusted with ethyl ethoxypropionate to a
15 solids content of 79.7%. The resulting polyesterdiol
has an acid number of 4.4 mg of KOH/g. The viscosity of
a 60% strength solution of the polyesterdiol in
ethoxyethyl propionate is 3.6 dPa.s at 23 degrees C.

20 **1.2.2. Preparation of the polyurethane dispersion**

749 g of the polyesterdiol according to Example
2, 6.6 g of 2-butyl-2-ethylpropanediol, 69 g of
dimethylolpropionic acid and 318 g of m-tetramethyl-
xylylene diisocyanate are charged to a 4 l steel
25 reactor which is suitable for the polyurethane resin
synthesis and are reacted at 110 degrees C until the
diisocyanate content is constant. Then 101 g of
trimethylolpropane are added and heating is continued
until the end of the reaction. Subsequently, 31.5 g of

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ethyl ethoxypropionate are added.

After stirring the reaction mixture for 30 minutes more, it is neutralized with 36.7 g of dimethyl-ethanolamine. The reaction mixture, which still has a
5 temperature of from 90 to 110 degrees C, is subsequently dispersed in 1929.2 g of water having a temperature of 60 degrees C.

The resulting polyurethane dispersion is free from gel particles, has a solids content of 36.1%, an acid
10 number of 30.3 mg of KOH/g and a pH of 7.1. At a temperature of 40 degrees C, the polyurethane dispersion is stable on storage for more than 4 weeks.

**Example 1.3: Preparation of the dispersion of a poly-
15 acrylate resin (A1) for component (III)**

385 g of n-butanol are charged to a 4 l steel reactor with stirrer, reflux condenser, two monomer feeds and an initiator feed, and are heated to 110 degrees C. Then, over the course of 5 hours, a monomer
20 mixture of (a1), (a2) and (a6):

(a1): 225 g of n-butyl methacrylate,

197 g of methyl methacrylate,

113 g of lauryl methacrylate

(commercial product Methacrylester 13 from Röhm
25 GmbH, Darmstadt),

(a2): 215 g of hydroxyethyl acrylate and

(a6): 181 g of styrene

is metered in.

Beginning simultaneously, a mixture of 68 g of tert-butyl peroxyhexanoate in 159 g of n-butanol is metered in over the course of 5.5 hours.

5 3.5 hours after the first monomer feed has been started, a second monomer feed is commenced which consists of a mixture of (a2) and (a3):

10 (a2): 113 g of hydroxyethyl methacrylate and
 (a3): 58 g of acrylic acid,

which feed is over after 1.5 hours.

Following the neutralization of the reaction mixture with 63 g of dimethylethanolamine and the 15 addition of 38 g of ethyl ethoxypropionate, the mixture is stirred for 30 minutes.

Then 1338 g of deionized water are added and the organic solvent is removed by distillation under reduced pressure down to a residual content of < 1.5% 20 by weight.

Following adjustment of the solids content to 39.9%, the dispersion is characterized. The number-average molecular weight Mn of the polyacrylate is 5017 daltons, the weight-average molecular weight Mw is 25 14,337 daltons. The acid number of the polyacrylate dispersion is 41.4 mg of KOH/g and the pH is 7.2. The

- 60 -

polyacrylate dispersion is stable on storage at 40 degrees C for more than 4 weeks.

Example 1.4: Preparation of coating components (I),

5 (II) and (III)

1.4.1. Preparation of component (I)

Component (I) is prepared from the constituents indicated below by mixing using a stirrer (600 10 revolutions per minute):

14.0 parts by weight of organic water-dilutable acrylate resin (A1) according to Example 1.1.

15 3.6 parts by weight of butylglycol acetate,
 3.0 parts by weight of butylglycol,
 1.0 part by weight of wetting agent (Tensid S,
 Biesterfeld),
 0.2 part by weight of leveling agent based on a
20 polyether-modified dimethyl-
 siloxane copolymer (Byk® 331 from
 Byk Gulden) and
 0.6 part by weight of leveling agent (Fluorat ® FC
 430 from 3M)

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1.4.2. Preparation of component (II)

Component (II) is prepared from the constituents indicated below by mixing using a stirrer (600 revolutions per minute):

5

2.9 parts by weight of polyisocyanate based on hexamethylene diisocyanate allophanate (Desmodur® VPLS 2102 from Bayer AG),

10 10.7 parts by weight of polyisocyanate based on hexamethylene diisocyanate trimer (Tolonate® HDTLV from Rhone-Poulenc) and

1.6 parts by weight of ethyl ethoxypropionate.

15

1.4.3. Preparation of component (III)

Component (III) is prepared from the constituents indicated below by mixing using a stirrer (600 revolutions per minute):

20

29.0 parts by weight of deionized water,

0.45 part by weight of dimethylethanolamine,

1.9 parts by weight of thickening agent based on polyurethane (Dapral® T210 from Akzo),

25

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8.9 parts by weight of polyacrylate dispersion (A1)
according to Example 1.3 with a
solids content of 38% and
17.5 parts by weight of polyurethane dispersion (A3)
5 according to Example 1.2 with a
solids content of 36%.

Example 1.5: Preparation of the novel clearcoat

The novel clearcoat is prepared by mixing
10 components (I), (II) and (III) using a stirrer (600 revolutions per minute), incorporating component (II) into component (I) by stirring and incorporating, by stirring, the resulting mixture into component (III).

**Comparison Example 1: Preparation of the clearcoat by an
15 alternative mixing technique**

The clearcoat of Comparison Example 1 is prepared by mixing components (I), (II) and (III) using a stirrer (600 revolutions per minute), incorporating component (I) into component (III) by stirring and then 20 incorporating, by stirring, component (II) into the mixture of (I) and (III).

**Comparison Example 2: Preparation of the clearcoat by an
alternative mixing technique**

25 The clearcoat of Comparison Example 2 is prepared by mixing components (I), (II) and (III) using

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a stirrer (600 revolutions per minute), incorporating component (III) into component (I) by stirring and then incorporating, by stirring, component (II) into the mixture of (I) and (III).

5

Example 1.6: Application of the clearcoats according to Example 1.5 and according to Comparison Examples 1 and 2 and testing of the baked coating films

10 A water-dilutable basecoat composition pigmented with aluminum flakes, according to EP-A-279 813, is applied to a phosphatized steel panel coated with a commercial electrodeposition coating and a commercial filler, so as to give a dry film thickness
15 of from 12 to 15 µm. The applied basecoat composition is dried at room temperature for 10 minutes and at 60°C for 10 minutes. Then the topcoat compositions according to Example 5 and to Comparison Examples 1 to 3 [sic] are sprayed onto the basecoat in 3 spray passes with a
20 flash-off time of 15 minutes in between. The panel is finally dried at room temperature for 60 minutes and baked at 60°C for 30 minutes in a convection oven. The multilayer coatings thus obtained were subjected to a number of tests, the results of which are shown in
25 Table 1.

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Table 1: Properties of the coatings produced in accordance with Example 6:

Coating according to

	Example 5	Comparison Examples 1	Examples 2
Degree of gloss ¹⁾ at 20 degrees	87	78	78
Coat thickness (micrometers)	50	61	60
Optical qualities (Visual)	clear	cloudy	gloss haze
Evenness (Visual)	very good	very poor	poor

¹⁾ Degree of gloss determined in accordance with DIN

5 67 530

Example 2: Preparation of a pigmented topcoat

Example 2.1: Preparation of the pigmented component (I)

10

2.1.1. Preparation of the organically dissolved polyurethane resin (A3) for component (I)

Preparation of the polyester precursor:

15 459.4 g of a dimeric fatty acid with the tradename Pripol® 1013, 133.9 g of cyclohexanedimethanol, 896.5 g of neopentylglycol hydroxypivalate, 21.3 g of butylethylpropanediol, 486.7 g of neopentylglycol 1262.4 g of isophthalic acid and 83.2 g

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of cyclohexane as entraining agent are weighed into a 4 l steel reactor suitable for polycondensation reactions.

The initial charge is then heated and the water of condensation is removed continuously to an acid number < 4.5. The batch is cooled to about 100 degrees C and adjusted with ethyl ethoxylpropionate [sic] to a solids content of 79.7%. The resulting polyesterdiol has a number-average molecular weight Mn of 2374 daltons and a weight-average molecular weight Mw of 4606 daltons (measured by GPC against polystyrene standard), a Gardner color number of less than 4, and an acid number of 4.4 mg of KOH/g. The viscosity of a 60% strength solution of the polyesterdiol in ethyl ethoxylpropionate is 3.3 dPas at 23 degrees C.

Preparation of the organically dissolved polyurethane resin (A3):

1860.0 g of the polyesterdiol precursor, 20 131.2 g of dimethylolpropionic acid, 26.7 g of butylethylpropanediol and 608.0 g of m-tetramethylxylylene diisocyanate are charged to a 4 l steel reactor suitable for the polyester resin synthesis and are reacted at 115 degrees C until the diisocyanate content is constant at 1.3%, when 120.8 g of trimethylolpropane are added and heating is continued

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until the reaction is over. Then 1028.8 g of isopropoxypopropanol are added.

After the reaction mixture has been stirred for 30 minutes more, it is neutralized with 69.6 g of N,N-dimethylethanolamine and cooled. Finally, it is adjusted to a solids content of 60% with isopropoxypopropanol.

The resulting polyurethane resin in organic solution has an acid number of 24.8 mg of KOH/g and a viscosity 10 in ethoxyethyl propionate of 6.2 dPas at 23 degrees C. The number-average molecular weight Mn of the polyurethane resin is 2529 daltons, the weight-average molecular weight Mw is 13,466 (measured by GPC against polystyrene standard).

15

2.1.2 Preparation of the pigmented component (I)

12 parts by weight of Paliogen blue, 50 parts of the 60% strength, neutralized polyurethane resin solution according to Example 2.1.1., 23 parts by 20 weight of butylglycol and 15 parts by weight of isobutanol are mixed with stirring and the mixture is dispersed with a sand mill.

2.2. Preparation of the dispersion of a polyacrylate 25 resin (A1) for component (III)

470 g of n-butanol are charged to a 4 l steel

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reactor with stirrer, reflux condenser, two monomer feeds and an initiator feed, and are heated to 110 degrees C. Then, over the course of 5 hours, a monomer mixture of (a1), (a2) and (a6):

5

- (a1): 240 g of n-butyl methacrylate
209 g of methyl methacrylate,
120 g of lauryl methacrylate
(Commercial product Methacrylester 13 from Röhm
10 GmbH, Darmstadt),
(a2): 270 g of hydroxyethyl methacrylate and
(a6): 180 g of styrene

is metered in.

- 15 Beginning simultaneously, a mixture of 36.0 g of tert-butyl peroxyethylhexanoate in 92.4 g of n-butanol is metered in over the course of 5.5 hours.
3.5 hours after the first monomer feed was started, a second monomer feed is commenced, consisting of a
20 mixture of (a2) and (a3):

- (a2): 120 g of hydroxyethyl methacrylate and
(a3): 61 g of acrylic acid,

25 and is over after 1.5 hours.

Following the neutralization of the reaction

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mixture with 63 g of dimethylethanolamine, it is stirred for 30 minutes. Then 1379 g of deionized water are added and the organic solvent is distilled off under reduced pressure down to a residual content of 5 less than 1.5% by weight.

After adjusting the solids content to 38.9%, the dispersion is characterized. The acid number of the polyacrylate dispersion is 37.2 mg of KOH/g and the pH is 7.4. The polyacrylate dispersion is stable on 10 storage at 40 degrees C for more than 4 weeks.

Example 2.3: Preparation of the application-ready topcoat

41.4 parts by weight of the pigmented component 15 (I) according to Example 2.1 are mixed thoroughly with a mixture of 19 parts by weight of a low-viscosity isophorone diisocyanate trimer and 7.5 parts by weight of a hexamethylene diisocyanate trimer (Desmodur® VPLS 2102) as component (II).

20 The complete premix of components (I) and (II) is added to 66.1 parts by weight of a mixture of:

4.5 parts by weight of ethyl ethoxypropionate,
4.5 parts by weight of dipropylene glycol mono-butyl ether,

25 0.2 part by weight of leveling assistant (Byk® 325 from Byk Gulden),

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0.2 part by weight of slip additive (Tegoglide®
410 from Goldschmidt AG),

0.8 part by weight of solvent (Solvesso® 200),

0.4 part by weight of butylglycol,

5 31.5 parts by weight of the polyacrylate dis-
persion (A1) according to
Example 2.2 and

24.0 parts by weight of deionized water.

10 Finally, 15 parts by weight of deionized water are
added to this mixture.

Annex 1: New set of claimsPatent claims:

5 1. Coating composition comprising at least three components, based on a polymer which contains hydroxyl groups and acid groups which can be converted into the corresponding acid anion groups and is dissolved or dispersed in one or more organic solvents, and on an
10 isocyanate group-containing crosslinking agent,
characterized in that

1.) component (I) contains as binder (A)

(A1) at least one acrylate copolymer (A1) which is
15 dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and
20 30,000 daltons, an OH number of from 40 to 200 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or

(A2) at least one polyester resin (A2) which is
25 dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups, which can be converted into the corresponding

acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 30 to 250 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and/or

- 5 (A3) at least one polyurethane resin (A3) which is dissolved or dispersed in one or more organic, optionally water-dilutable solvents and contains hydroxyl groups and acid groups,
- 10 which can be converted into the corresponding acid anion groups, having a number-average molecular weight Mn of between 1000 and 30,000 daltons, an OH number of from 20 to 200 mg of KOH/g and an acid number of from 5 to 150 mg of KOH/g, and
- 15 (A4) if desired, at least one water-dilutable binder from the group of the acrylicized polyurethane resins and/or polyester-acrylates which is compatible with the other constituents of component (I),

20 the binder components (A1), (A2), (A3) and, optionally, (A4) being selected such that a 50% strength solution of the binder (A) in ethoxyethyl propionate has a viscosity of \leq 6.0 dPa.s at 23°C,

25 2.) component (II) comprises as crosslinking agent (F)

at least one di- and/or polyisocyanate (F1) which is optionally dissolved or dispersed in one or more organic solvents, and, optionally, at least one further crosslinking agent consisting of at 5 least one epoxide compound (F2) having at least two epoxide groups per molecule and/or at least one amino resin (F3), and

3.) component (III) comprises components (A1) and/or 10 (A2) and/or (A3) and/or (A4) in aqueous dispersion.

2. Coating composition according to claim 1, characterized in that

15 1.) as component (A1), acrylate copolymers are employed which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of <= 6.0 dPa.s at 23 degrees C, and/or

20 2.) as component (A2), polyester resins are employed which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of <= 6.0 dPa.s at 23 degrees C, and/or

25 3.) as component (A3), polyurethane resins are employed which, as a 50% strength solution in ethoxyethyl propionate, have a viscosity of <= 6.0 dPa.s at 23 degrees C, and/or

4.) in that the binders (A1) and/or (A2) and/or (A3) and/or (A4) are selected such that a 50% strength

solution of the binder (A) in ethoxyethyl propionate has a viscosity of \leq 6.0 dPa.s at 23 degrees C.

5 3. Coating composition according to claim 1 or 2, characterized in that component (I) comprises as binder (A) at least 20% by weight of (A1), from 0 to 30% by weight of (A2), from 0 to 80% by weight of (A3) and from 0 to 10% by weight of (A4), the sum of the
10 proportions by weight of components (A1) to (A4) being in each case 100% by weight, based on the binder (A).

4. Coating composition according to one of claims 1 to 3, characterized in that (A1) is obtainable by
15 polymerizing, in an organic solvent or a solvent mixture, and in the presence of at least one polymerization initiator,

- a1) an acid-group-free (meth)acrylic ester which is
20 different from (a2), (a3), (a4), (a5), and (a6) and is copolymerizable with (a2), (a3), (a4), (a5), and (a6), or a mixture of such monomers,
- a2) an ethylenically unsaturated monomer which carries
25 at least one hydroxyl group per molecule and is free from acid groups, which is copolymerizable with (a1), (a3), (a4), (a5), and (a6) and is different from (a5), or a mixture of such monomers,

- a3) an ethylenically unsaturated monomer which carries at least one acid group which can be converted into the corresponding acid anion group per molecule and is copolymerizable with (a1), (a2),
5 (a4), (a5), and (a6), or a mixture of such monomers, and
- (a4) if desired, one or more vinyl esters of α -branched monocarboxylic acids having 5 to 18 carbon atoms per molecule,
- 10 a5) if desired, at least one reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of an α -branched monocarboxylic acid having 5 to 18 carbon atoms per molecule or, instead of the reaction product, an equivalent quantity of acrylic and/or methacrylic acid, which is then reacted, during or after the polymerization reaction with the glycidyl ester of an α -branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, and
- 15 a6) if desired, an acid-group-free, ethylenically unsaturated monomer which is copolymerizable with (a1), (a2), (a3), (a4), and (a6) and is different from (a1), (a2), (a4) and (a5), or a mixture of such monomers,
- 20
25 (a1), (a2), (a3), (a4), (a5), and (a6) being selected in nature and quantity such that the polyacrylate resin (A1) has the desired OH number, acid number and the

desired molecular weight.

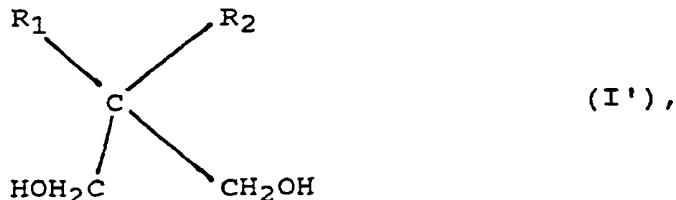
- 5. Coating composition according to one of claims 1 to 4, characterized in that the polyester resin (A2) 5 is obtainable by reacting

p1) polycarboxylic acids or esterifiable derivatives thereof, together if desired with monocarboxylic acids,

- 10 p2) polyols, together if desired with monoools,
- p3) if desired, further modifying components, and
- p4) if desired, a component which is reactive with the reaction product of (p1), (p2) and, if used, (p3).

- 15 6. Coating composition according to one of claims 1 to 5, characterized in that the polyurethane resin (A3) is obtainable by employing an alcohol component which consists, at least in a certain proportion, of

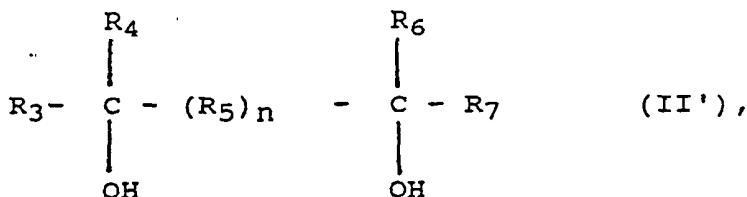
- 20 a₁) at least one diol of the formula (I')



in which R₁ and R₂ are each an identical or different radical and are an alkyl radical of 1 to 18 carbon atoms, an aryl radical or a

cycloaliphatic radical, with the proviso that R₁ and/or R₂ may not be methyl, and/or

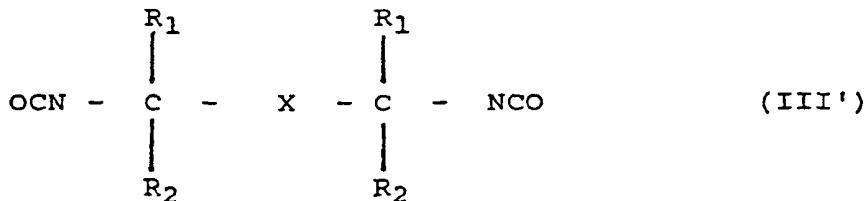
a₂) at least one diol of the formula (II')



5

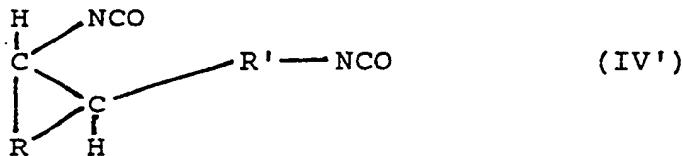
in which R₃, R₄, R₆ and R₇ are each identical or different radicals and are an alkyl radical of 1 to 6 carbon atoms, a cycloalkyl radical or an aryl radical, and R₅ is an alkyl radical of 1 to 6 carbon atoms, an aryl radical or an unsaturated alkyl radical of 1 to 6 carbon atoms, and n is either 0 or 1,

and/or by employing diisocyanates of the general
15 formula (III'):



in which X is a divalent, aromatic hydrocarbon radical, preferably an optionally halogen, methyl- or methoxy-substituted naphthylene, diphenylene or 1,2-, 1,3- or
20 1,4-phenylene radical, particularly preferably a 1,3-phenylene radical, and R₁ and R₂ are an alkyl radical of

1 to 4 carbon atoms, preferably a methyl radical,
and/or by employing diisocyanates of the general
formula (IV'):



5 where: R is a divalent alkyl or aralkyl radical of 3
to 20 carbon atoms and
R' is a divalent alkyl or aralkyl radical of 1
to 20 carbon atoms.

10 7. Coating composition according to one of claims
1 to 6, characterized in that component (II) comprises,
as crosslinking agent,

(F1) at least 70% by weight, preferably from 80 to 100%
15 by weight, of a nonblocked di- and/or
polyisocyanate (F1) and/or of a mixture of blocked
and nonblocked di- and/or polyisocyanate,
(F2) from 0 to 30% by weight, preferably from 2 to 20%
by weight, of at least one epoxide compound (F2)
20 having at least 2 epoxide groups per molecule, and
(F3) from 0 to 30% by weight, preferably from 2 to 20%
by weight, of at least one amino resin (F3),

based in each case on the overall weight of the
25 crosslinking agent (F).

8. Coating composition according to one of claims
1 to 7, characterized in that component (I) consists of
- (A) from 20 to 90% by weight, preferably from 35 to
5 80% by weight, of the binder (A),
- (B) from 0 to 60% by weight of at least one pigment
and/or filler,
- (C) from 5 to 50% by weight, preferably from 10 to 40%
10 by weight, of at least one organic, optionally
water-dilutable solvent, and
- (D) from 0 to 20% by weight, preferably from 2 to 10%
by weight, of at least one neutralizing agent
- (E) from 0 to 20% by weight, preferably from 2 to 10%
15 by weight, of at least one customary auxiliary
and/or additive,

the sum of the proportions by weight of components (A)
to (E) being in each case 100% by weight, and component
(II) consists of

- 20 (F) from 50 to 100% by weight, preferably from 60 to
90% by weight, of at least one crosslinking agent
(F),
- (G) from 0 to 50% by weight, preferably from 10 to 40%
25 by weight, of at least one organic, optionally
water-dilutable solvent, and
- (H) from 0 to 20% by weight, preferably from 0 to 10%
by weight, of at least one customary auxiliary

and/or additive,

the sum of the proportions by weight of components (F) to (H) being in each case 100% by weight, and component
5 (III) consists of

- (J) from 40 to 90% by weight, preferably from 50 to 85% by weight, of water,
- (K) from 5 to 50% by weight, preferably from 10 to 45% by weight, of components (A1) and/or (A2) and/or (A3) and/or (A4) of the binder (A) in water-dispersed form,
- (L) from 0 to 20% by weight, preferably from 2 to 10% by weight, of at least one neutralizing agent, and
- 15 (M) from 0 to 20% by weight, preferably from 2 to 10% by weight, of at least one customary auxiliary and/or additive,

the sum of the proportions by weight of components (J) to (M) being in each case 100% by weight.

9. Coating composition according to one of claims 1 to 8, characterized in that components (I), (II) and (III) are present in quantities such that the ratio of 25 equivalents of hydroxyl groups of components (A1) and/or (A2) and/or (A3) and/or (A4) of the binder (A) to the crosslinking groups of the crosslinking agent (F) is between 1:2 and 2:1, preferably between 1:1.2

and 1:1.5.

10. Process for the preparation of the coating compositions according to one of claims 1 to 9,
5 characterized in that first of all a solution of the binder (A) is prepared in the organic, optionally water-dilutable solvent, the further constituents of component (I) are dispersed in this binder solution, and the resulting component (I) is then mixed with the
10 components (II) and, if desired, (IV), and subsequently the mixture obtained is added to component (III).

11. Process for the preparation of the coating compositions according to one of claims 1 to 9, charac-
15 terized in that first of all a solution of the binder (A) is prepared in the organic, optionally water- dilutable solvent, the further constituents of component (I) are dispersed in this binder solution, and the resulting component (I) is then mixed with
20 components (II) and, if desired (IV), and subsequently component (III) is added to the resulting mixture.

12. Use of the coating compositions according to one of claims 1 to 9 in repair coating, especially in
25 automotive refinishing.

13. Use of the coating compositions according to one of claims 1 to 9 for the coating of plastics.

14. Use of the coating compositions according to one of claims 1 to 9 as topcoat and/or filler.

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